

Effect of Length of Chopped Pristine and Intercalated Graphite Fibers on the Resistivity of Fiber Networks

(NASA-TM-101395) EFFECT OF LENGTH OF
CHOPPED PRISTINE AND INTERCALATED GRAPHITE
FIBERS ON THE RESISTIVITY OF FIBER NETWORKS
(NASA) 13 p CSCI 11D

N89-11820

G3/24 Unclass
0174593

James R. Gaier
Lewis Research Center
Cleveland, Ohio

and

Mark Stahl
Cleveland State University
Cleveland, Ohio

Prepared for the
Fall Meeting of the Materials Research Society
Boston, Massachusetts, November 28—December 2, 1988



EFFECT OF LENGTH OF CHOPPED PRISTINE AND INTERCALATED GRAPHITE

FIBERS ON THE RESISTIVITY OF FIBER NETWORKS

James R. Gaier
National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

and

Mark Stahl
Cleveland State University
Cleveland, Ohio 44115

SUMMARY

Samples of Amoco P-100 fibers were chopped to lengths of 3.14, 2.53, 1.90, 1.27, 0.66 mm, or milled for 2 hr. The two-point resistivity of compacts of these fibers were measured as a function of pressure from 34 kPa to 143 MPa. Samples of each fiber length were intercalated with bromine at room temperature and similarly measured. The low pressure resistivity of the compacts decreased with increasing fiber length. Intercalation lowered the resistivity of each of the chopped length compacts, but raised the resistivity of the milled fiber compacts. Bulk resistivity of all samples decreased with increasing pressure at similar rates. Even though fiber volumes were as low as 5 percent, all measurements exhibited measurable resistivity. A greater change with pressure in the resistance was observed for shorter fibers than for longer, probably an indication of tighter fiber packing. Intercalation appeared to have no effect on the fiber to fiber contact resistance.

INTRODUCTION

Probably the first widespread electrical applications of intercalated graphite fibers will not be as direct conductors (such as cabling) but as enhancers to low conductivity materials. In these applications the difficult problems of interconnection between the fibers and conventional conductors is avoided. Such schemes usually envision using chopped fibers embedded in a matrix. As examples, there have been promising reports of the electromagnetic interference shielding of intercalated graphite fiber - polystyrene composites (ref. 1), and efforts are underway to try to improve the lightning-strike tolerance of carbon fiber epoxy matrix aircraft skin this way.

In a previous study, however, it was found that if graphite fibers are reduced to very small lengths (on the order of a few microns) by milling, their bulk resistivity increases dramatically over the single fiber value (ref. 2). Further, when bromine intercalated fibers were used, the resistivity of the milled fibers was similar or perhaps even higher than that of the pristine fibers. This was attributed to the degassing of bromine from the newly created fiber surfaces (ref. 3).

There are many unanswered questions about the transverse resistivity of the fibers, the fiber to fiber contact resistance, and the percolation of electrical current through a network of fibers which are relevant to the application of chopped, intercalated graphite fibers. This prompted us to further investigate the effects of length on the bulk resistivity of pristine and intercalated graphite fibers.

METHODS AND MATERIALS

The high modulus pitch-based fibers (Amoco P-100) used in this study were chopped to 3.14, 2.53, 1.90, 1.27, or 0.66 mm lengths by stretching out several tows on a hard rubber mat, and chopping them with a row of properly spaced blades mounted on a hydraulic press. This resulted in relatively uniform length fibers, as shown in figure 1(a), with none being longer than the spacing and only a small percentage shorter due to breakage. Other samples of the fibers were milled for 2 hr in an isopropanol medium according to previously reported procedures (ref. 2).

Samples of each of the chopped lengths and of the milled fibers were exposed to approximately 165 torr of bromine vapor at room temperature for at least 24 hr. Previous studies have shown that this is sufficient time for intercalation of the pitch-based fibers under these conditions (ref. 4). The procedure for milled fibers differed from that in the previous study (ref. 2); in that study fibers were intercalated and then milled, and in this study the order was reversed. Intercalating the already chopped or milled fibers also assures that the initial length distribution of the fibers should be the same because the samples were drawn from the same batch. Thus, any changes in the fracture behavior of the fibers due to intercalation would not influence the initial size distribution.

The two-point resistivities of the samples were measured by filling an insulated die, shown in figure 2, of 0.124 in. (3.15 mm) diameter with 10 mg of fibers. Both the anvil and the piston were electrical conductors (beryllium-copper) and provided the electrical contacts. Pressure was applied up to 1.28 MPa using weights, and up to 143 MPa using a hydraulic press. Height was monitored using a digital cathetometer mounted on a height gauge. Resistance measurements were made using a constant current source and a nanovoltmeter. The contact surfaces were cleaned and sanded after each use.

RESULTS AND DISCUSSION

Pristine Fibers

At the pressure caused by the piston weight (34 kPa), good electrical contact was established. Bulk resistivity of the samples at three different pressures is shown in table I. The low pressure resistivity increased as the fiber length decreased. Resistivities ranged from 0.5 Ω -cm for the 3.14 mm fibers to 3.4 Ω -cm for the milled fibers. The resistivity value for the milled fiber is considerably higher than the 0.05 Ω -cm value reported earlier using a different measurement technique (ref. 2). Although this is a two-point measurement, the resistance due to the apparatus was less than 0.1 percent of the resistance measured at this pressure. The magnitude of the fiber to fiber, and the fiber

to apparatus contact resistance is uncertain and may account for the discrepancy.

Resistivity of the sample decreased with increasing pressure (fig. 3(a)). The decreases in the low pressure region (up to about 1 MPa) were, to a first approximation, linear on a log-log scale with the slope having a slight dependence on length, ranging from about -0.3 for the 3.14 mm fibers to about -0.9 for the milled fibers. In the high pressure region the length dependence tends to disappear, and a slope of about -0.4 is observed. At 140 MPa, the resistivity varied from 15 to 43 m Ω -cm for the chopped fibers and was 79 m Ω -cm for the milled.

In this apparatus an increase in pressure means a decrease in sample height. A look at the geometrical constraints of the cylinder is revealing. Figure 4(a) shows the normalized resistivity (resistivity, ρ / initial resistivity, ρ_0) of the compact as a function of percent fiber volume. The initial resistivity is the resistivity measured at the lowest pressure, that caused by the weight of the piston. At the lowest pressure, the chopped fibers occupied between 5 and 10 percent of the sample volume and the milled about 23 percent. As the sample volume is decreased the fibers can rearrange, bend, and break to decrease the void volume in the sample. At 100 MPa, the volume occupied by the fibers had increased to 25 to 35 percent for the chopped and 40 percent for the milled, and by 140 MPa the fibers occupied essentially all of the volume. The increasing volume percent of fibers would cause the bulk resistivity to decrease.

The diameter of the cylinder was about the same as the longest fiber lengths (3.15 mm). As the height of the cylinder was reduced to less than the 3.14 mm, some fiber breakage must occur. This is confirmed in figure 1(b), which shows the chopped fibers after a measurement. Very few fibers did not undergo breakage.

One would expect that the increase in the number of broken fibers might cause the bulk resistivity of the sample to increase. It could also be argued that the increased number of parallel current paths might cause a resistivity decrease. As can be seen in figure 5(a), the resistivity of the sample dropped continuously across the entire range of heights. The slope of the log resistivity, however, did make an abrupt downward change. All of the fibers with lengths greater than 1 mm show a similar curve, with a dramatic change in slope when the sample height was near half of the fiber length. The 0.66 mm fibers, however, showed an abrupt change in slope near 1.2 times the fiber length. Perhaps at this fiber length the absolute sample height (0.8 mm) is small enough that the breakage is dominated by sample pore volume effects rather than by the "must break" height. Although fiber breakage must increase the resistivity of the sample, the more intimate contact forced upon the fibers by the increased pressure and the decreasing void volume were evidently more important in determining the bulk resistivity of the sample.

Bromine Intercalated Fibers

The resistivity for shorter fibers is expected to be higher than that of longer fibers because bromine is depleted from all surfaces of the fiber. Thus a shorter fiber will have a lower percentage of the fiber which is intercalated. A simple model was used to calculate the magnitude of the expected

effects of fiber length on the resistivity. The bromine is assumed to deplete completely to a depth of 2 μm around its perimeter (refs. 2 and 5). If one assumes 10 μm diameter fibers, that leads to an intercalated core 6 μm in diameter. If one assumes that depletion in the axial direction is also 2 μm , then particles with a length less than 4 μm should be fully deintercalated. Assuming a resistivity of 50 $\mu\Omega\text{-cm}$ for the intercalated lengths and 250 $\mu\Omega\text{-cm}$ for the pristine lengths, results of the calculation for each of the fiber lengths used in this study are shown in table II. Note that fibers 0.66 mm long should have resistivities about 2 percent higher than the 3.14 mm fibers. According to this rough calculation, it should be difficult to detect differences between these extremes in lengths of the chopped fibers caused by fiber deintercalation at the fracture surfaces.

The bulk resistivities of the chopped bromine intercalated P-100 fibers at 34 kPa pressure was indeed lower than that of the corresponding pristine fibers (fig. 3). As shown in table I, the factor of improvement varied from a factor of 2.5 to a factor of 9.8 and did not scale with length. Since these resistivity differences are much larger than those predicted from the length effect model, and since they did not have a strong length dependence, only a small portion of the length dependence of the resistivity can be attributed to the depletion of bromine from the fiber ends.

One would expect that the resistivity of the milled then intercalated fibers would not be reduced because the particle sizes are, for the most part, less than the 4 μm deintercalation layer. Experimentally, the resistivity of the milled fibers increased upon intercalation by a factor of 10. This resistivity increase can be attributed to damaging the fibers through the intercalation-deintercalation process (ref. 2).

As the pressure was increased the resistivity of the intercalated fiber decreased (fig. 3(b)). With fibers having lengths of 1.27 mm and longer, there was no appreciable differences in the slope of the log resistivity versus log pressure curve. The slope was also similar to that observed for the pristine fibers in the low pressure region (less than 1 MPa), though slightly flatter in the high pressure region (-0.35). The 0.66 mm length fibers, however, showed an increased slope in the low pressure region. The milled, intercalated P-100 fibers, which had higher resistivities than the pristine, also had a similar slope in the low pressure region but a flatter slope (-0.15) at high pressure.

Bromination seems to have little, if any, effect on the breakage of the intercalated P-100 fibers as evidenced by comparing the resistivity change with column height (fig. 5(b)). One would expect that the change in the resistivity versus height slope would occur at a different height if the breakage differed, and that did not happen. One would also expect that as the fibers deintercalated at each fracture, the total volume of intercalated fibers would be decreasing (and the total volume of the pristine fibers increasing) as the height of the cylinder decreased. There was evidence for that. At very high pressure the slope of the resistivity versus height (fig. 5) was slightly shallower for the intercalated fibers than for their pristine counterparts which is consistent with the fiber resistivity of the intercalated fibers increasing with fracture.

Percolation and Contact Resistance

Since this is a two-point measurement, the resistance includes factors other than the sample and can be expressed as:

$$R_{\text{meas}}(L) = R_{\text{device}} + R_{\text{dev-fib}} + R_{\text{sample}}(L)$$

where $R_{\text{meas}}(L)$ is the measured resistance, R_{device} is the resistance due to the measurement apparatus, $R_{\text{dev-fib}}$ is the total contact resistance between the measurement apparatus and the fibers, and $R_{\text{sample}}(L)$ is the total resistance of the sample.

$R_{\text{sample}}(L)$ is a function of the resistance of the individual fibers, R_{fiber} , and of the total contact resistance between the fibers $R_{\text{fib-fib}}(L)$. $R_{\text{fib-fib}}(L)$, and also $R_{\text{sample}}(L)$ and $R_{\text{meas}}(L)$, are functions of fiber length because for shorter fibers the current must travel through more fibers as it percolates through the sample. Contact resistance increases with the number of fiber-fiber interfaces that carriers must travel through, and so with decreasing length of the fibers.

Previous measurements have shown that the resistivity of the pristine and bromine intercalated P-100 fibers shows almost no variation with pressure at least to 630 MPa (ref. 6). Breakage of the fibers is expected to increase the resistivity of the fibers. Yet, the resistivity of the bulk fibers decreased with pressure. This implies that the resistivity changes are dominated by the change in the void volume and by the contact resistance.

Since the resistivity is not a function of length in the pristine fibers, and to a first approximation in the intercalated fibers (because the deintercalation volume is small), changes in the resistance of compacts that are fiber length dependent are indicative of the fiber to fiber contact resistance or percolation effects.

If the effect of void volume could be treated using a simple rule of mixtures, the void volume component of the resistivity would be a straight line between the initial and final volumes. Electrical resistance, however, will be limited by percolation effects. Far below the percolation limit, the resistivity will be similar to that of the matrix (air in these experiments). Far above the percolation limit, which should be low because of the high aspect ratio of the fibers, the resistance should drop slowly with fill factor.

All of the data showed a steep decline in the resistivity within the first few percent of void volume decrease. This implies that the percolation threshold must be below 5 percent fiber volume for the chopped fibers and less than 23 percent fiber volume for milled. Since the matrix is air, gravity and packing may constrain these "composites" to be above their percolation limit, since each fiber can only be supported by another fiber.

If the low void volume data are considered, then any percolation effects can certainly be ignored. This implies that differences in resistivity with fiber length must be dominated by contact resistance. Figure 4 shows that at low void volumes (high fiber volumes) the normalized resistivity, ρ/ρ_0 , decreased as length decreased. This indicates a greater change in contact resistance with pressure for shorter fibers than for longer. This is probably

due to the tighter packing of shorter fibers as the height of the sample decreases.

Bromine intercalation of the fibers had little, if any, effect on the contact resistance. This is not surprising in light of the absence of bromine on the surface of the fibers. One would expect, however, as breakage occurs the resistivity of the smaller fibers to be slightly larger than their longer counterparts because of the length effect on the intercalated volume. This becomes important at very low void volumes when many of the fibers are fractured to lengths below the 0.004 mm limit. Thus, the resistivity differences should be slightly larger than their pristine counterparts. This expectation is born out in figure 4.

CONCLUSIONS

It has been found that the resistivity of a network of graphite fibers decreases as the pressure on that network increases. A greater change with pressure in the resistance was observed for longer fibers than for shorter, probably an indication of greater fiber breakage. Intercalation lowers the low pressure resistivity of the network, but only produces small changes in its response to pressure. The effects of intercalation decrease as the fiber length decreases. These small deviations are consistent with degassing of the intercalate at each new fiber fracture surface. The dominant factor affecting the resistivity of the network was found to be void volume. Intercalation appeared to have no effect on the fiber to fiber contact resistance.

REFERENCES

1. M.A. Centanni and E. Clark, Graphite Intercalation Compounds, Extended Abstracts, M.S. Dresselhaus, G. Dresselhaus, and S.A. Solin, eds., p. 219, Materials Research Society, Pittsburgh, PA (1986).
2. J.R. Gaier, M.E. Dillehay, and P.D. Hambourger, J. Mater. Res., 2, 195, (1987).
3. X.W. Qian, S.A. Solin, and J.R. Gaier, Phys. Rev. B 35, 2436 (1987).
4. J.R. Gaier, Synth. Met., 22, 15 (1987).
5. D.A. Jaworske, 17th Biennial Conference on Carbon: Extended Abstracts and Program, p. 77, American Carbon Society, St. Marys, PA (1985). Complete report is D.A. Jaworske and R. Zinolabedini, NASA TM-87015, 1985.
6. P.D. Hambourger, Private Communication.

TABLE I. - RESISTIVITY OF SAMPLES AT THREE
DIFFERENT PRESSURES

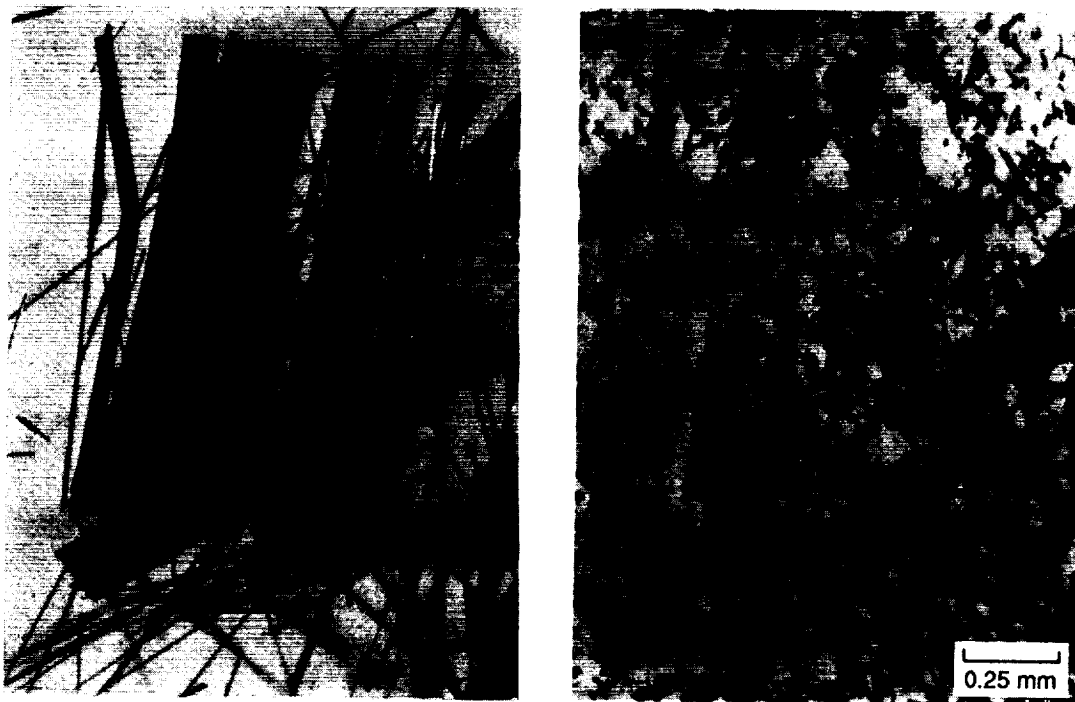
Length, mm	Type	Pressure		
		34 kPa	1.28 MPa	143 MPa
		Resistivity, Ω -cm		
3.14	Pristine ↓	0.492	0.139	0.022
2.53		.667	.207	.015
1.90		1.053	.201	.040
1.27		1.813	.263	.043
.66		1.925	.234	.023
(a)		3.383	.173	.079
3.14	Br ₂ intercalated ↓	0.192	0.051	0.028
2.53		.072	.029	.007
1.90		.108	.038	.010
1.27		.232	.044	.011
.66		.546	.045	.009
(a)		37.56	.597	.091

^aMilled.

TABLE II. - CALCULATED SINGLE FIBER
RESISTIVITIES FOR FIBERS OF
VARIOUS LENGTHS

Fiber length, mm	Percent brominated	Resistivity, $\mu\Omega$ -cm	R/R _∞
(a)	100.00	50.00	1.000
3.17	99.87	52.25	1.005
2.53	99.84	50.32	1.006
1.90	99.79	50.42	1.008
1.27	99.69	50.63	1.012
.66	99.39	51.21	1.024
.01	60.00	130.00	2.600
≤.004	.00	250.00	5.000

^aInfinite.



(A) BEFORE.

(B) AFTER.

FIGURE 1. - PHOTOMICROGRAPH OF P-100 FIBERS CHOPPED TO A UNIFORM LENGTH BY THE TECHNIQUE DESCRIBED IN TEXT BEING SUBJECTED TO 143 MPa.

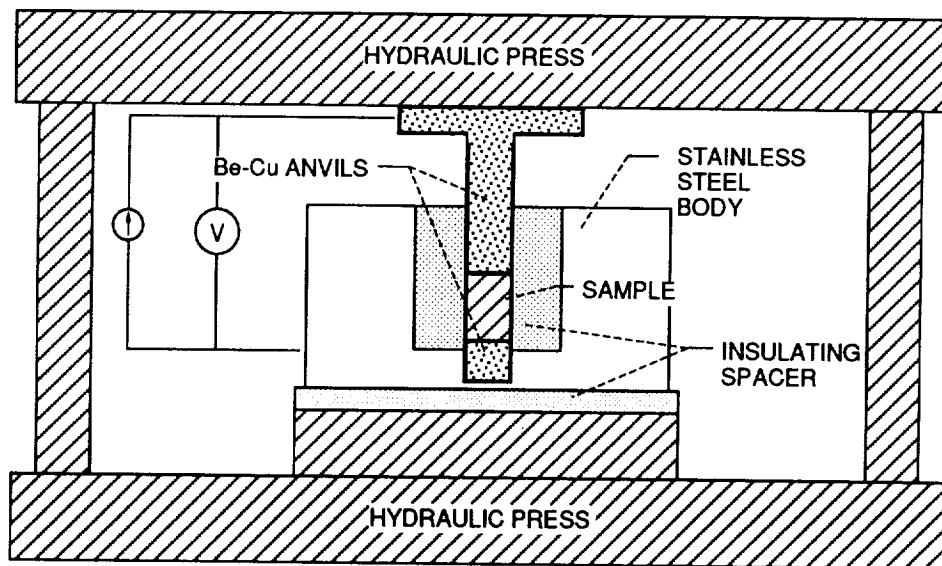


FIGURE 2. - APPARATUS USED TO MEASURE THE RESISTANCE OF A FIBER COMPACT AS A FUNCTION OF PRESSURE.

ORIGINAL PAGE IS
OF POOR QUALITY

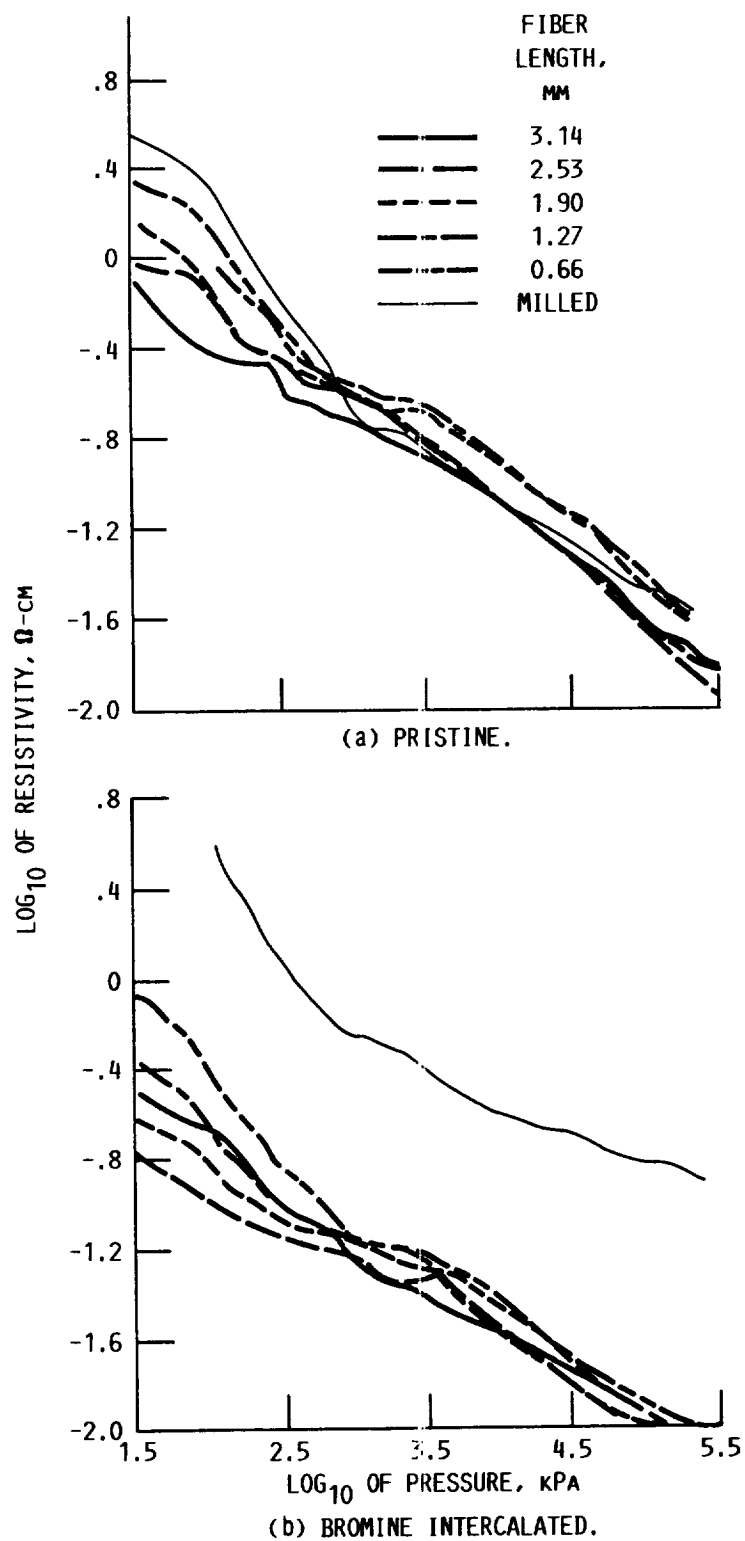


FIGURE 3. - THE LOG₁₀ OF THE BULK RESISTIVITY IN Ω-CM OF PRISTINE AND BROMINE INTERCALATED P-100 FIBERS OF VARIOUS LENGTHS AS A FUNCTION OF THE LOG₁₀ OF THE APPLIED PRESSURE IN KPA.

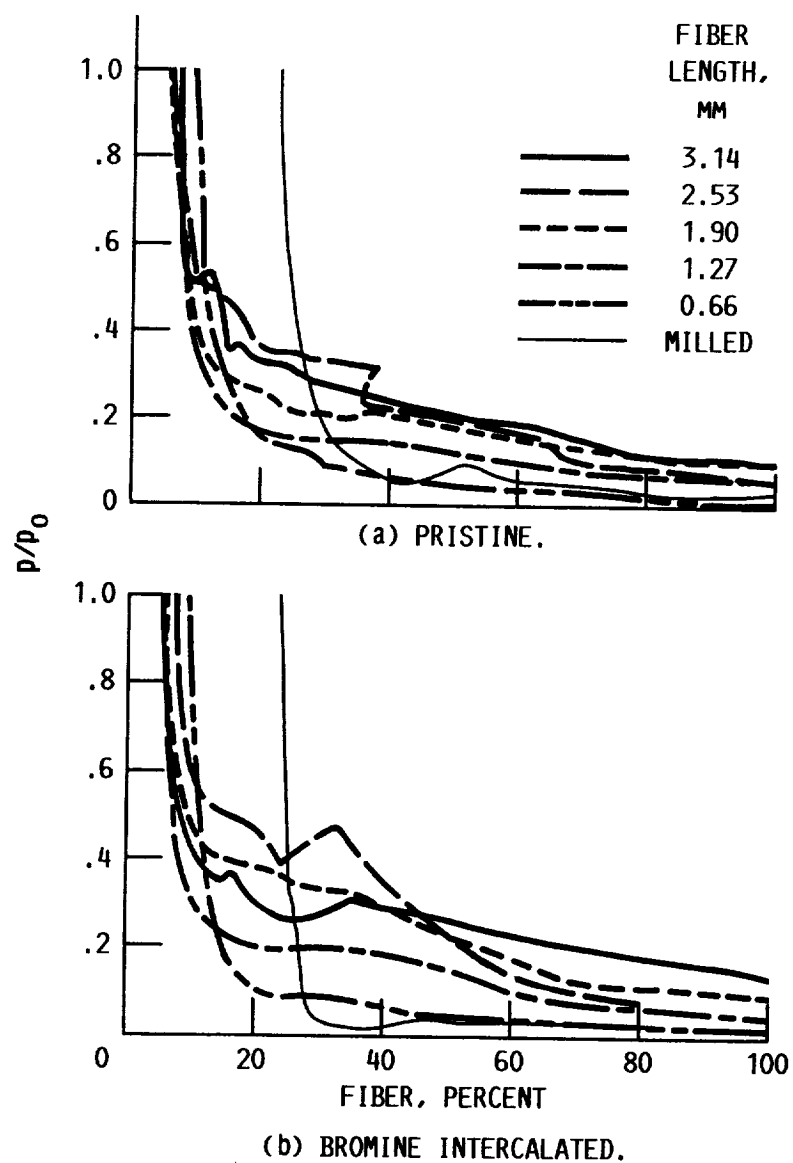


FIGURE 4. - THE NORMALIZED BULK RESISTIVITY (p/p_0) AS A FUNCTION OF PRISTINE AND BROMINE INTERCALATED P-100 FIBERS AT VARIOUS LENGTHS AS A FUNCTION OF PERCENT FIBER VOLUME.

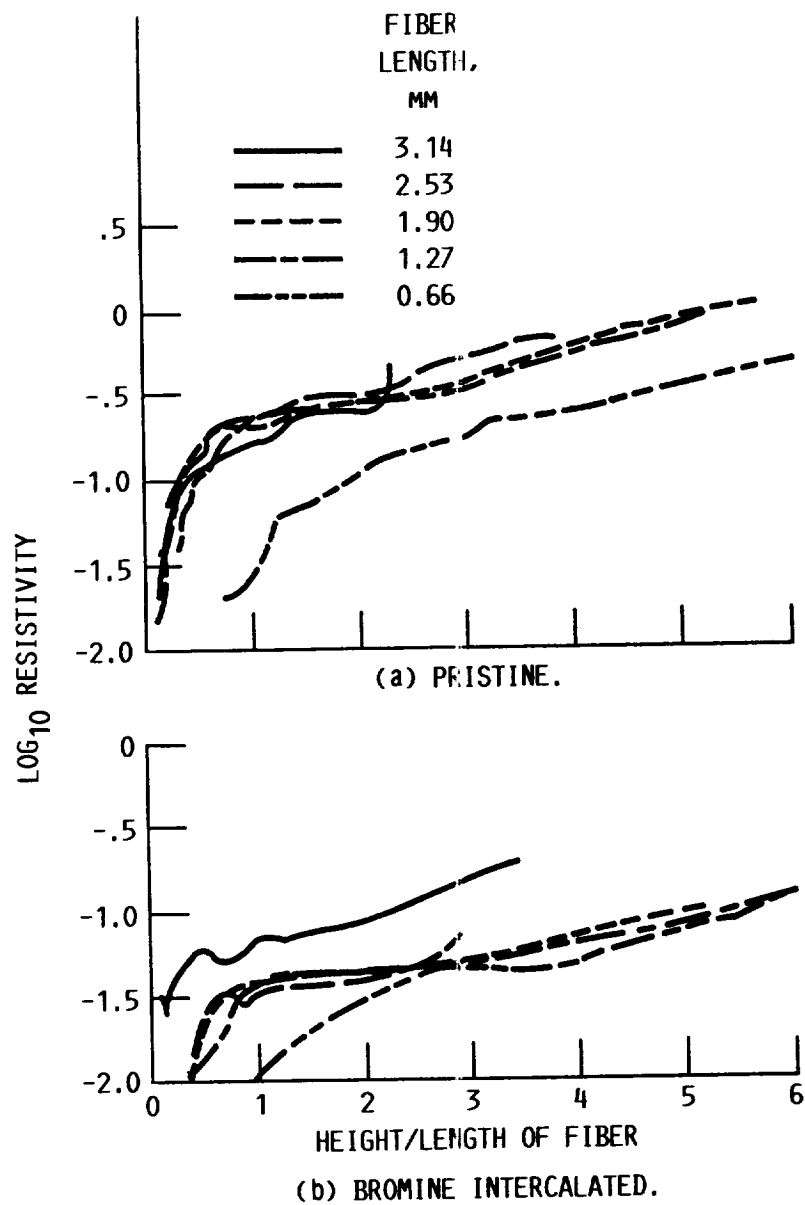


FIGURE 5. - THE LOG_{10} OF THE BULK RESISTIVITY IN $\Omega\text{-cm}$ OF PRISTINE AND BROMINE INTERCALATED P-100 FIBERS OF VARIOUS LENGTHS AS A FUNCTION OF THE SAMPLE HEIGHT/FIBER LENGTH.

Report Documentation Page

1. Report No. NASA TM-101395		2. Government Accession No.		3. Recipient's Catalog No.	
4. Title and Subtitle Effect of Length of Chopped Pristine and Intercalated Graphite Fibers on the Resistivity of Fiber Networks				5. Report Date	
				6. Performing Organization Code	
7. Author(s) James R. Gaier and Mark Stahl				8. Performing Organization Report No. E-4474	
				10. Work Unit No. 141-20-00	
9. Performing Organization Name and Address National Aeronautics and Space Administration Lewis Research Center Cleveland, Ohio 44135-3191				11. Contract or Grant No.	
				13. Type of Report and Period Covered Technical Memorandum	
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546-0001				14. Sponsoring Agency Code	
15. Supplementary Notes Prepared for the Fall Meeting of the Materials Research Society, Boston, Massachusetts, November 28—December 2, 1988. James R. Gaier, NASA Lewis Research Center; Mark Stahl, Cleveland State University, Cleveland, Ohio 44115.					
16. Abstract Samples of Amoco P-100 fibers were chopped to lengths of 3.14, 2.53, 1.90, 1.27, 0.66 mm, or milled for 2 hr. The two-point resistivity of compacts of these fibers were measured as a function of pressure from 34 kPa to 143 MPa. Samples of each fiber length were intercalated with bromine at room temperature and similarly measured. The low pressure resistivity of the compacts decreased with increasing fiber length. Intercalation lowered the resistivity of each of the chopped length compacts, but raised the resistivity of the milled fiber compacts. Bulk resistivity of all samples decreased with increasing pressure at similar rates. Even though fiber volumes were as low as 5 percent, all measurements exhibited measurable resistivity. A greater change with pressure in the resistance was observed for shorter fibers than for longer, probably an indication of tighter fiber packing. Intercalation appeared to have no effect on the fiber to fiber contact resistance.					
17. Key Words (Suggested by Author(s)) Graphite fibers Graphite intercalation compounds Chopped fibers Resistivity of fiber networks				18. Distribution Statement Unclassified—Unlimited Subject Category 24	
19. Security Classif. (of this report) Unclassified		20. Security Classif. (of this page) Unclassified		21. No of pages 12	
				22. Price* A03	